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(54) **Color concentrates for thermoplastic polymeric materials.**

(57) A color concentrate for coloring thermoplastic polymeric materials, which is prepared from a blend of a water - or organic solvent-dispersible polymer and a heat-stable, chemically-inert coloring agent selected from water-soluble dyes, organic-soluble dyes, polymer-soluble dyes, and pigments, from which blend any solvent present during processing is subsequently removed.

BACKGROUND OF THE INVENTIONField of the Invention

This invention relates generally to the coloring of thermoplastics. In particular, it relates to the coloring of thermoplastics by the incorporation of color concentrates therein.

Prior Art

The coloring of thermoplastic articles by incorporation of pigments introduced as color concentrates is well known. Likewise, the coloring of synthetic thermoplastic fibers by absorption of dye from solution is also a common procedure. However, coloring of fibrous materials through the use of color concentrates is a less common practice. The reasons for this are many fold. It is imperative that the degree of dispersion of pigmentary particles in the concentrate be very high so that the spinning process will not be interrupted. On the other hand, preparation of masterbatches of dye concentrate, which would not have such a dispersion problem, by a chip dyeing procedure is complicated and expensive. Furthermore, the majority of color concentrates available today contain vehicles which are not totally compatible with, for instance, nylon, since nylon is one of the fibers which is less commonly colored by the addition of color concentrates.

Described here is the preparation of pigment or dye concentrates in vehicles which are compatible with common fiberforming thermoplastic materials, in particular nylon. The procedure is simple and very flexible. It can be used to prepare concentrates of pigments or water - or solvent - soluble dyes, starting from dry colorant powders or from presscakes or aqueous or solvent dispersions. The concentrates can be used to

color thermoplastic materials using blending techniques or melt injection of concentrate into polymer streams. The degree of dispersion is very good, so the concentrates can be used to color fibrous as well as more dimensionally uniform objects.

Advantages of the instant system over those described in the prior art are a result of the advantages of employing a polymer which is soluble in water and/or in organic solvents:

A.) Water

Pigments and dyes are precipitated from aqueous reaction mixtures during manufacture. Pigments are very finely divided at this point. Subsequent drying agglomerates pigment, and this is undesirable. Having a polymer which is water soluble allows for easy incorporation of pigment into polymer by mixing polymer solution and pigment dispersion and drying. Water soluble dyes can also be incorporated with no dispersion problem whatsoever and with very high color yields.

B.) Organic Solvent

There are classes of dyes which are very soluble in certain organic solvents. Having a polymer soluble in these polar organic solvents enables one to make high concentration concentrates with no dispersion problem and with very high color yields.

Statement of Closest Known Art

1. U.S. 1,119,960. The essence of this process is a transfer of pigment from aqueous to "oil" phase. This is a three phase process - solid, aqueous and oil. The oil and the aqueous phase remain as two distinct

liquids. The present process is two phase - solid and one liquid. No surfactants are used. There is no concern about incomplete transfer of pigment, so no pigment is lost. There is no concern about partial miscibility of oil in water thus resulting in loss of some of the oil phase and contamination of the water. All of the instant polymer is recovered, and any water present is removed by drying.

Another advantage of the present system is that a thermoplastic color concentrate can be made with ease from a process performed completely at room temperature. If the process of the reference is done at room temperature, it is necessary that the oil phase be a liquid, and thus the resulting colored product is not suited for handling using conventional plastic extrusion equipment. If the oil phase is a thermoplastic, then the process must be carried out at elevated temperatures. This is undesirable and also presents problems of miscibility of the different phases, because of viscosity differences and too rapid drying of the aqueous phase.

Moreover, since the instant polymers are soluble in aqueous and polar organic solvents, one can incorporate dyes, both water soluble and solvent soluble, into such polymers at room temperature without going through a phase transfer process.

The degree of dispersion achieved in a solid concentrate in the process of the reference is usually limited to the degree of dispersion originally present in the presscake. In the present invention, it is a simple matter to disperse the colorant, either in pure solvent or in the polymer solution or dispersion, to any desired degree of dispersion.

2. U.S. 3,360,497. This reference uses a phase transfer process. However, since the final phase thereof is hydrophobic and is not soluble in water, a preliminary phase transfer step is required in order to transfer pigment from aqueous to hydrophobic phase. Complicated surfactants are needed. This hydrophobic dispersion is then combined with a solution of polymer in a hydrophobic solvent. In an embodiment of the present system, polymer is added directly to the aqueous dispersion. This simplifies matters greatly. No preliminary phase transfer step is necessary and no phase transfer surfactants are needed. The problems of incomplete transfer and other problems associated with phase transfer as mentioned above are eliminated. The referenced system would have utility with solvent soluble dyes, but transfer of colorant from aqueous phase to "oil" phase is still required; whereas the present system is a single liquid phase system.

SUMMARY OF THE PRESENT INVENTION

Difficulties resulting from the utilization of prior art processes and compositions are obviated by the provision of a color concentrate according to the present invention. This color concentrate is a blend of two essential components, advantageously a fluid - phase blend, from which blend any solvent present during processing is subsequently removed. The first component is a water - dispersible or organic solvent - dispersible polymer which is capable of being:

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(1) utilized in the preparation of a 1 - 95 % solution or dispersion;

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(2) recovered from a 1 - 95 % solution or dispersion thereof at a temperature which will not cause substantial volatilization or degradation thereof;

(3) fused at standard thermoplastic processing temperatures; that is, between about 130 and 350°C;

20

(4) melted with a thermoplastic material to be colored without substantial degradation or reaction and without any visible separation on a microscopic scale; and

(5) utilized as a wetting agent for pigments.

25

The second component is a heat - stable, chemically inert coloring agent selected from the group consisting of water - soluble dyes, organic - soluble dyes, polymer - soluble dyes, and pigments.

30

Especially advantageous results are achieved if the first component of the concentrate is selected from the group consisting of water - dispersible or organic solvent - dispersible polyamides; water - dispersible or organic solvent - dispersible polyesters; water -

dispersible or organic solvent - dispersible vinyl polymers or copolymers; and water - dispersible or organic solvent - dispersible alkylene oxide polymers or copolymers. Under such conditions, very beneficial results are obtained when the coloring agent is a pigment, which is present in the color concentrate in an amount sufficient to provide from about 1 to about 70 percent by weight thereof, based on the total weight of the color concentrate. Equally beneficial results are achieved, moreover, if the coloring agent is a dye, which is present in the color concentrate in an amount sufficient to provide from about 1 to about 70 percent by weight thereof, based on the total weight of the color concentrate.

Concentrates according to the present invention are utilized with especially advantageous results in coloring thermoplastic polymeric materials which are employed in the production of synthetic textile fibers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTSEXAMPLES

The following examples set forth in detail various methods of preparing and utilizing color concentrates according to the present invention. As is understood by those of skill in the art, these
5 examples are illustrative in nature, and should not be taken as limiting the invention in any way.

EXAMPLE 1

176 g of the water dispersible polyamide of USP
10 3,846,507 was combined with 704 g of water. The mixture was stirred at 80°C until dispersion of the polymer was complete.

200g of Hilton Davis Peacoline (copper phthalocyanine)
15 Blue 37.7% solids presscake was placed in a two quart stainless steel Waring blender. 80g of the aqueous polymer dispersion was added to the blender. The mixture was blended for 25 minutes. The remaining 800g of polymer dispersion was added in 200g increments with
20 approximately 10 minutes blending time between increments. Microscopic examination of the pigment slurry at this point revealed very good wetting of the pigment by the vehicle and dispersion of the pigment in the vehicle.

25 The slurry was then filtered through a 35mm screen pack assembly consisting of 4 filter screens: a 20 mesh, a 60 mesh, a 180 mesh, and a 325 mesh (40 micron) screen. One filter change was required. The slurry was
30 then collected in a shallow pan and dried under vacuum at 60°C until hard (approximately 2 days). This yielded a color concentrate containing 30% pigment.

One part of the solid color concentrate was blended with 29 parts of uncolored nylon-6 polymer containing 0.03% titanium dioxide. This mixture was extruded into yarn comprised of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meter/minute. This fiber was then drawtwisted at a draw ratio 3.4 to 1 at a speed of 400 meters/minute with a twist of 0.25 turns/inch to yield yarn containing drawn fiber of approximately 16 denier/filament. Deeply colored blue fiber containing 1% pigment was obtained.

EXAMPLE 2

The procedure of Example 1 was repeated except that the Hilton Davis Peacoline Blue 37.7% solids presscake was replaced by duPont Monastral Green G 53.4% high-solids presscake. Deeply colored green fiber containing 1% copper phthalocyanine green pigment was obtained.

EXAMPLE 3

The procedure of Example 1 was repeated except that the Hilton Davis Peacoline Blue presscake was replaced by BASF Paliofast LBGD-K 46.6% solids copper phthalocyanine blue presscake. Deeply colored blue fiber containing 1% pigment was obtained.

EXAMPLE 4

The procedure of Example 1 was repeated except that Hilton Davis Peacoline Blue presscake was replaced by duPont Monastral Green G GT-751-D dry powder copper phthalocyanine pigment and dispersion was accomplished ultrasonically using an ultrasonic dispersing device manufactured by Sonic Corp. (Stratford, CT.) to produce a concentrate containing 25% pigment. The concentrate was used as before to produce deeply colored green fiber.

EXAMPLE 5

The procedure of Example 1 was repeated except that Hilton Davis Peacoline Blue presscake was replaced by BASF Luconyl Red 387, a 30 percent dispersion of
5 Pigment Red 123 in water, and no high speed mixing was employed. One part of the 30 percent concentrate was blended with 29 parts of uncolored nylon 6 polymer containing 0 percent titanium dioxide, and the procedure of Example 1 was followed to produce deeply-colored
10 red fiber containing 1% pigment.

EXAMPLE 6

320g of BASF Neozapon Yellow R solvent-soluble dye was dispersed in 1067ml of anhydrous methanol. The colorant
15 dispersed (except for a small amount of residual insolubles) almost instantly and very little stirring was required.

480g of the polyamide of USP 3,846,507 was combined
20 with 2400g of a solvent which consisted of 300g of water and 2100g of methanol. The mixture was stirred at 50°C until dispersion of the polymer was complete.

The 17% polymer dispersion was added slowly to the
25 methanolic dispersion of Neozapon R with stirring. The resulting dispersion was then filtered through the filter pack assembly described in Example 1. Almost no pressure build-up on the screen pack was recorded. The dispersion was then placed in a shallow pan and
30 dried under vacuum at 50-60°C. 670g of a 40% color concentrate was obtained.

One part of the solid color concentrate was blended with 39 parts of uncolored nylon-6 polymer containing
35 0.03% titanium dioxide. The mixture was extruded into

fiber as in Example 1 to obtain deeply colored golden fiber containing 1% colorant.

EXAMPLE 7

- 5 6.5g of the nylon soluble colorant Filamid Red 841 (Ciby Geigy) was combined with 100g of a 20% aqueous dispersion of the polyamide of USP 3,846,507. The mixture was then removed from the heat and left undisturbed until the colorant completely dispersed.
- 10 The dispersion was filtered through the filter pack assembly described in Example 1. It was estimated that <3% of the original amount of colorant was deposited on the screen. The dispersion was dried in a vacuum oven at approximately 60°C to obtain a color concentrate
- 15 containing 25% pigment.

- One part of the solid color concentrate was blended with 24 parts of uncolored nylon-6 polymer containing 0.03% titanium dioxide. The mixture was extruded into
- 20 yarn comprised of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meters/minute. The yarn was then drawtwisted to yield deeply colored maroon fiber of 12 denier/filament.

25 EXAMPLE 8

The procedure of Example 7 was repeated except that Filamid Red 841 was replaced by Filamid Yellow 2732. Deeply colored golden fiber was obtained.

30 EXAMPLE 9

- The procedure of Example 1 was repeated except that American Hoechst pigment Novoperm Red BL was used, and the pigment was compounded directly into the molten polyamide of USP 3,846,507 using a high shear process
- 35 rather than dispersed into an aqueous dispersion of the

polymer using a high speed mixing process. A color concentrate containing 25% pigment was obtained. One part of this solid color concentrate was blended with 24 parts of uncolored nylon-6 polymer containing
5 0.03% titanium dioxide and spun and drawtwisted into yarn as described in Example 1. Deeply colored red fiber containing 1% pigment was obtained.

EXAMPLE 10

10 One part of the color concentrate of Example 2 was blended with 29 parts of uncolored poly(ethylene terephthalate) containing 0.33% titanium dioxide and spun into yarn comprised of fiber of 52 denier/filament at a temperature of 300°C and a spinning speed of
15 330 meters/minute. The yarn was drawtwisted as in Example 1 to yield deeply colored green fiber of 16 denier/filament, containing 1% pigment.

EXAMPLE 11

20 463g of Hilton Davis Peacoline (copper phthalocyanine) Blue 37.7% solids presscake was placed in a two quart stainless steel Waring blender. 715g of a 28.5% dispersion of the water-dispersible polyester of USP 4,098,741 was added to the blender and the
25 mixture was blended for one hour. An additional 715g of the polyester dispersion was added to the mixture and blending was continued for another hour. Microscopic examination of the pigment slurry at this point revealed good wetting of the pigment by the vehicle and
30 good dispersion of the pigment in the vehicle.

The slurry was then filtered through the 35mm screen pack described in Example 1. No filter changes were required. The slurry was collected in a shallow pan
35 and dried under vacuum at 60°C until hard. This yielded

a color concentrate containing 30% pigment. One part of the solid color concentrate was blended with 29 parts uncolored nylon-6 polymer containing 0.03% titanium dioxide. The mixture was extruded into yarn comprised
5 of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meters/minute. This yarn was then drawtwisted into fiber of 12 denier/filament to yield deeply colored blue fiber containing 1% pigment.

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EXAMPLE 12

One part of the color concentrate of Example 11 was blended with 29 parts of uncolored poly(ethylene terephthalate) containing 0.33% titanium dioxide and
15 spun into yarn comprised of fiber of 52 denier/filament at a temperature of 300°C and a spinning speed of 330 meters/minute. The yarn was drawtwisted to yield fiber of 16 denier/filament. Deeply colored blue fiber containing 1% pigment was obtained.

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EXAMPLE 13

One part of the color concentrate of Example 11 was blended with 29 parts of the uncolored poly(ethylene terephthalate) containing no titanium dioxide and spun
25 into yarn comprised of fiber of 52 denier/filament at a temperature of 300°C and a spinning speed of 330 meters/minute.

The yarn was drawtwisted to yield fiber of 12 denier/filament. Deeply colored blue fiber containing 1%
30 pigment was obtained.

EXAMPLE 14

142g of duPont Monastral Green G GT-751-D dry powder copper phthalocyanine pigment was placed in a two
35 quart stainless steel Waring blender. 750g of a

- 28.5% dispersion of the water dispersible polyester of USP 4,098,741 was added to the blender and the mixture was blended for 1 hour. An additional 750g of polymer dispersion was added and blending was continued for an
5. additional hour. Microscopic examination of the pigment slurry revealed good wetting of the pigment by the vehicle and good dispersion of the pigment in the vehicle. The slurry was filtered through the screen pack assembly described in Example 1. One filter change
- 10 was made during the filtering. The slurry was collected in a shallow pan and dried in a vacuum oven at 50°C until hard. A color concentrate containing 25% pigment was obtained.
- 15 One part of the solid color concentrate was blended with 24 parts of uncolored poly(ethylene terephthalate) containing 0.33% titanium dioxide and spun into yarn comprised of fiber of 52 denier/filament at a temperature of 300°C and at a spinning speed of 330 meters/minute.
- 20 The yarn was drawtwisted as in Example 1 to yield a fiber of 16 denier/filament. Deeply colored green fiber containing 1% pigment was obtained.

EXAMPLE 15

- 25 400g of the sodium salt of a low molecular weight vinyl copolymer consisting of the monomers 2-sulfoethyl methacrylate and ethyl acrylate in a ratio of 1 sulfonated monomer to every 4 non-sulfonated monomers was combined with 400g of water. The polymer dissolved rapidly to
- 30 yield a clear yellow liquid which appeared to be more of a true polymer solution than a dispersion as was obtained in the previous examples.

- 454.7g of Hilton Davis Peacoline (copper phthalocyanine)
- 35 Blue 37.7% solids presscake was placed in a two quart

stainless steel Waring blender. 400g of the polymer solution was added to the blender and the mixture was blended for 45 minutes. The remaining polymer solution was added and the mixture was blended for an additional
5 45 minutes.

The pigment slurry was then filtered through the screen pack assembly described in Example 1 with one filter change required. The material was collected in a stainless steel beaker and dried under vacuum at 40-70°C
10 until hard. A color concentrate containing 30% pigment was obtained.

One part of the solid color concentrate was blended with 29 parts of uncolored nylon-6 polymer containing
15 0.03% titanium dioxide. This mixture was extruded into yarn comprised of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meters/minute.

A sulfur-like odor was noticed during spinning and
20 extrusion of uncolored vinyl polymer with nylon-6 causing a slight discoloration of the nylon. Also, some crocking of the blue colorant onto guides on the fiber takeup machine was noticed. The spun yarn was draw-twisted as described in Example 1 to yield fiber
25 of 16 denier/filament. Deeply colored blue fiber containing 1% pigment was obtained.

EXAMPLE 16

400g of a primarily poly (alkylene oxide) polymer such
30 as those disclosed in U.S. 4,093,676 or U.S. 4,029,694, was combined with 2266g of water and the mixture was heated and stirred until the polymer became dispersed homogeneously in the water solvent. The mixture was blended in a Waring blender briefly to insure homo-
35 geneity.

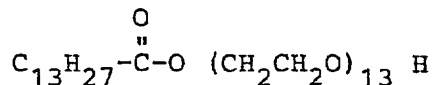
606g of Hilton Davis Peacoline (copper phthalocyanine) Blue 37.7% solids presscake was placed in a two quart stainless steel Waring blender. 500g of the polymer dispersion was added to the blender and the mixture
 5 was blended for 1 hour. The remaining 2166 g of polymer dispersion were added to the pigment slurry in four equal increments and the mixture was blended for 30 minutes after each addition. Microscopic examination of the pigment slurry revealed good wetting of the pigment
 10 by the vehicle and good dispersion of the pigment in the vehicle.

The pigment slurry was filtered through the filter pack assembly described in Example 1. Three filter changes
 15 were required. The slurry was collected in a shallow pan and dried under vacuum at 50-60°C until dry. A color concentrate containing 36% pigment was obtained.

One part of the solid color concentrate was blended
 20 with 35 parts of uncolored nylon-6 polymer containing 0.03% titanium dioxide. The mixture was extruded into yarn comprised of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meters/minute. This yarn was then drawtwisted as in
 25 Example 1 to yield deeply colored blue fiber of 16 denier/filament.

EXAMPLE 17

40.2g of duPont Monastral Green G GT-751-D dry powder
 30 copper phthalocyanine pigment, 6.0g of the surfactant:



and 160.0g of demineralized water were charged into a
 35 two quart stainless steel Waring blender. The mixture

was blended for 30 minutes and then filtered through the filter assembly described in Example 1.

75g of nylon-6 polymer containing no titanium dioxide
5 was dissolved in 300g of formic acid at a temperature near the boiling point of formic acid.

The pigment slurry was heated to 90°C and added slowly to the hot polymer solution. The resulting slurry was
10 collected in a shallow pan and allowed to sit undisturbed for 2 days. Upon cooling, a solid material was obtained. This solid material was broken into smaller pieces and placed in a vacuum oven at 60°C until dry. A color concentrate containing 22% pigment was obtained.

15 One part of the solid color concentrate was blended with 21 parts of uncolored nylon-6 polymer containing 0.03% titanium dioxide. The mixture was extruded into yarn comprised of fiber of 52 denier/filament at a
20 temperature of 255°C and a spinning speed of 330 meters/minute. This yarn was then drawtwisted as in Example 1 to yield deeply colored green fiber of 16 denier/filament.

25 EXAMPLE 18

194g of the water dispersible polyamide of USP 3,846,507 was combined with 775g of water. The mixture was stirred at 80°C until dispersion of the polymer was complete.

30 83g of Ciba-Geigy Nylaspin Scarlet G heat stable, water soluble dye was added to the aqueous polymer dispersion. As the mixture was stirred, the dye particles dissolved and went into solution forming a deep maroon-colored liquid. The viscosity of the polymer dispersion in-
35 creased as the dye particles dissolved. Heating to 40°C

accelerated the dissolution process.

Microscopic examination of the dye solution revealed a deeply and uniformly colored liquid containing a
5 small number of insoluble particles, the particles being present in the original dye powder.

The solution/dispersion was filtered through the filter pack assembly described in Example 1 and dried in a
10 vacuum oven at 60°C to obtain a thermoplastic color concentrate containing 30% colorant.

One part of the solid color concentrate was blended with 29 parts of uncolored nylon-6 polymer containing
15 0.03% titanium dioxide. The mixture was extruded into yarn comprised of fiber of 52 denier/filament at a temperature of 255°C and a spinning speed of 330 meters/minute. This yarn was then drawtwisted as in Example 1 to yield drawn fiber of approximately 16
20 denier/filament. Deeply colored brownish-orange fiber containing 1% colorant was obtained.

The present invention has been described in detail with respect to certain preferred embodiments thereof.
25 As is understood by those of skill in the art, variations and modifications in this detail may be effected without any departure from the spirit and scope of the present invention, as defined in the hereto-appended claims.